

Thermal decomposition and kinetic studies of solid riboflavin using model-free methods

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ABSTRACT

The thermal stability and decomposition kinetics of riboflavin were investigated by nonisothermal thermogravimetric analysis (TGA) experiments in an inert atmosphere. For kinetic analysis, riboflavin was heated from room temperature to 800 °C with five different heating rates (5,10,15,20 and 30°C min⁻¹). From the thermal decomposition process, it was found that there are two main stages of pyrolysis. In the DTG thermograms, the temperature peaks at maximum weight loss rate changed with varying heating rate. The kinetic parameters of decomposition including apparent activation energy (E_a) and $\ln A$ (pre-exponential factor) under an inert atmosphere have been evaluated from the model-free isoconversion methods of Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO) and Friedman over the whole temperature domain. It was found that values of E_a and $\ln A$ decrease with increasing conversion (α). The reaction order does not have a significant influence on the process because of the high value of the pre-exponential factor. The apparent activation energy distributions with conversion calculated by these methods ranged between 15.18 and 236.55 kJ mol⁻¹, and varied over a broad range in a complex manner depending on the heating rate.

KEYWORDS: riboflavin, nonisothermal degradation, solid-state kinetics, isoconversional methods

1. INTRODUCTION

Riboflavin (vitamin B₂) has conjugated double bonds and nitrogen in its ring structure and commercially can be produced by chemical synthesis or microbial fermentation [1, 2]. It is present in most living systems, and in milk, eggs, meat products and vegetables [3] which are essential for normal growth and development of the body, production and regulation of essential hormones, and

formation of red blood cells [4]. Moreover, riboflavin has an essential role in metabolising carbohydrates, proteins, lipids, and is crucial for the development of biological energy in the electron-transport system. Riboflavin is an active part of the coenzymes of flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD), which catalyse various redox reactions and play central roles in several dehydrogenases and oxidases.

The process of thermal decomposition, primarily involving temperature and heating rate, influences riboflavin in food processing. It is relatively stable during thermal food processing and various food storage conditions but in the presence of light it can be very easily reduced and oxidised by accepting or donating an electron or hydrogen atom [5]. The investigation of the kinetics and reaction mechanisms of solid compounds is a demanding task with complex results arising from a great variety of features such as the formation and growth of new nuclei, diffusion of reaction products, and the physical state of the reagents [6]. In recent decades thermo analytical methods of analysis (TGA, DTA, DSC) have become the most frequently used techniques to study a variety decomposition reactions of solids, e.g. lifetime prediction, characterizing the processes of transformation of solids, or the participation of solids in processes of isothermal or nonisothermal heating, and the estimation of the kinetic and thermodynamic parameters of these processes [7-11]. Today, qualitatively and quantitatively, thermal analysis is an important tool for research and development in materials science. The determination of kinetic parameters, such as the rate of reaction, apparent activation energy and pre-exponential factor, by nonisothermal isoconversional methods offers advantages over conventional isothermal studies because it defines the complex nature of the solid-state heterogeneous reaction. The usefulness of isoconversional analysis lies in its ability to disclose and treat the complexity of the respective processes. The evaluation of the apparent activation energy at progressive degrees of conversion is always a subject matter for vibrant discussions among investigators. All this curiosity lies in the fact that the value of the apparent activation energy can provide a picture about the optimum reaction conditions for the synthesis of various kinds of materials. Moreover, it gives an idea about the thermal stability and the expected longevity of solid materials to be kept at a certain temperature. The kinetic information is obtained by conducting multiple experiments at different heating rates by various kinetic methods. The application of model-free methods is highly recommended in order to obtain a reliable kinetic explanation of the process investigated.

However, to our knowledge, the thermal stability and degradation of riboflavin have not been studied systematically. Maslowska *et al.* established the thermal decomposition of riboflavin by thermogravimetry technique in a static air atmosphere at various heating rates, calculated kinetic parameters such as activation energy, reaction order, pre-exponential and reaction rate constant, and a proposed reaction mechanism for the thermal decomposition of riboflavin [12,

13]. We now report the thermal stability and thermal decomposition process in a helium atmosphere and the resulting kinetic parameters for the degradation of riboflavin. The objective of this paper was to study the potential of model-free isoconversional methods to provide clues about the decomposition mechanism of riboflavin and to investigate the kinetics of its thermal degradation over a range of temperature. The nonisothermal TG data was treated by three model-free isoconversional methods namely two integral methods, i.e. Kissinger–Akahira–Sunose (KAS) [14,15] and Flynn–Wall–Ozawa (FWO) [16,17] and one differential method i.e. Friedman [18] for evaluating the variation of the apparent activation energy (E_a) and pre-exponential (frequency) factor ($\ln A$) within the degree of conversion (α) investigated.

2. EXPERIMENTAL

Instrumentation and material

Nonisothermal TGA, and its first derivative DTG, analyses of riboflavin (Merck, 99.5%, m.p. 220°C, powder) were carried out in a SDT 2960 simultaneous TG/DTG unit from Q 500 TA Instruments USA under a helium atmosphere at a purge rate of 10.0 mL min⁻¹. A sample about 1g mass was used for the experiments at five different heating rates (β) of 5, 10, 15, 20 and 30°C min⁻¹ upto 800°C. Open alumina crucibles were used at all heating rates. Temperature, baseline and weight calibrations were carried out for each heating rate. The TGA and DTG curves were recorded simultaneously with 0.1 mg sensitivity.

Isoconversional method

The TG/DTG method is very useful for the determination of decomposition temperature, and kinetic parameters for solid materials. The kinetics of thermal degradation reactions are described with various equations taking into account the special features of their mechanisms. According to the results of the International Congress on Thermal Analysis and Calorimetry (ICTAC) kinetic project, isoconversional methods give more reliable kinetic information than other methods [19]. Isoconversional methods can be used to calculate kinetic parameters without modelling assumptions [20,21], and reveal the complexity of the process in the form of a functional dependence of activation energy (E_a) on the extent of conversion (α) [22-24]. The basic assumption of these methods is the reaction rate for a constant degree of conversion depends only on the temperature [22]. To use these methods, a series of experiments has to be performed at different heating rates [14-25]. The knowledge of E_a versus α allows the detecting of multi-step processes and predicting the reaction scheme [26] over a wide temperature range. Of nonisothermal kinetics, the Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO) and Friedman methods are the most popular representatives of the isoconversional approach.

Kissinger–Akahira–Sunose (KAS) method

The KAS method [14, 15] is based on the Coats–Redfern [27] approximation which is based on the following equation:

$$\ln\left(\frac{\beta}{T^2}\right) = \frac{\ln AR}{E_a g(\alpha)} - \frac{E_a}{RT} \quad (1)$$

where, E_a is apparent activation energy, A is the pre-exponential factor, and T is the absolute temperatures, R is the universal gas constant, β is the heating rate and $g_{(\alpha)}$ is the integral conversion function (reaction model).

For constant α , a plot of $\ln(\beta/T^2)$ versus $1000/T$ is a straight line whose slope is E_a/RT and intercept is $\ln AR/E_a g_{(\alpha)}$.

Flynn–Wall–Ozawa (FWO) method

The FWO method [16, 17] is based on the following equation:

$$\ln \beta = -1.052(E_a/RT) + [\ln(AE_a/R) - \ln(g(\alpha)) - 5.33] \quad (2)$$

It is used to determine the apparent activation energy for given values of conversion. The activation energy for different conversion values can be calculated from a plot of $\ln \beta$ versus $1000/T$ whose intercept is $\ln AE_a/R$.

Friedman method

The Friedman method [18] is most general of the differential techniques and utilises the following natural logarithmic equation:

$$\ln\left(\beta \frac{d\alpha}{dt}\right) = \ln A + \ln f(\alpha) - \frac{E_a}{RT} \quad (3)$$

By plotting $\ln(\beta d\alpha/dt)$ against $1000/T$ for a constant α value, the value of $-E_a/R$ can be obtained directly. This method is accurate because it does not include any mathematical approximations.

3. RESULTS AND DISCUSSION**TGA data analysis**

The TG, and its first derivative DTG, curves of the decomposition process of riboflavin obtained at five heating rates are shown in Figure 1(a and b), referring to decomposition in a narrow temperature range. From Figure 1a, it can be observed that the residual weight after thermal degradation increases with increasing heating rate, which reflects the increase in thermal stability. In TGA experiments there was neither significant peak detection nor weight loss observed below 150 °C, confirming the absence of moisture content in the riboflavin. In a helium atmosphere two weight-loss steps occur during thermal degradation. The first major degradation step of riboflavin occurs in a temperature range of 250–350 °C whereas, above 350 °C, the

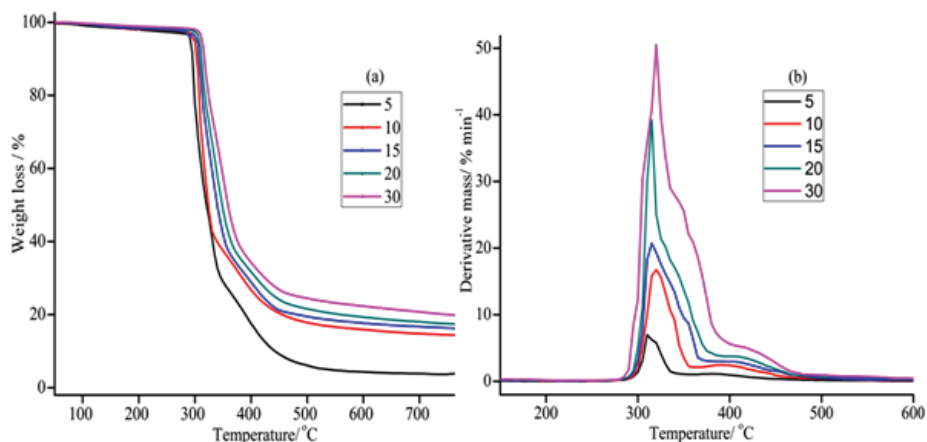


Figure 1 (a) TGA and (b) DTG curves for the thermal decomposition process of riboflavin in helium atmosphere.

second minor degradation step is observed. The first thermal degradation step of riboflavin mainly occurs at the ribo block, accompanied with the formation of alcohol, ethylene and acetaldehyde [13], whereas the second degradation is attributed to the degradation of the flavin block accompanied with the formation of CO_2 , phenol and finally char formation. As can be seen in the DTG curves (Figure 1b), there is a shift in conversion lines caused by the effects of varying heating rates. At the lower heating rate, the DTG peaks appear first, while at higher heating rates, the peak areas are broader, and the conversion curves are shifted to higher temperatures. The maximum rate of weight loss of the two stages shifts to higher temperatures, and the decomposition rate increases, as the heating rate increases from 5 to 30 $^{\circ}\text{C min}^{-1}$. The shift of the TG/DTG curves to higher temperature with increasing heating rate could be attributed to the short time required for a sample to reach a given temperature at the high heating rate due to heat transfer limitations [28]. At the same heating rate, it was found that $T_{\text{max}1}$ is higher than $T_{\text{max}2}$. Nonisothermal experimental conditions and analysis criteria such as onset temperatures and their weight loss, endset temperatures and their weight loss, the temperatures of maximum rates of thermal degradation (T_{max}) and their percentage maximum weight loss rate (α_{max}), are summarised in Table 1. The subscripts 1 and 2 represent the first and second steps of the degradation, respectively. Briefly all these characteristics are shifted to higher values as the heating rate is increased.

Isoconversional kinetic analysis

In order to contribute to a deeper comprehension role of various heating rates ($\beta = 5, 10, 15, 20, 30$ $^{\circ}\text{C min}^{-1}$) on the thermal degradation of riboflavin, the apparent activation energy (E_a) and pre-exponential factor ($\ln A$) at several degrees of conversion (α) were calculated by applying the KAS, FWO and Friedman isoconversional methods. These methods could be applied by determination

Table 1 TG–DTG phenomenological data for riboflavin under helium atmosphere at five heating rates

Heating rate (β)	Step 1							Step 2				
	T_{on} ($^{\circ}C$)	Wt. loss (%)	T_{end} ($^{\circ}C$)	wt loss (%)	T_{max1} ($^{\circ}C$)	α_{max1} (wt% min $^{-1}$)	T_{on} ($^{\circ}C$)	wt loss (%)	T_{end} ($^{\circ}C$)	wt loss (%)	T_{max2} ($^{\circ}C$)	α_{max2} (wt% min $^{-1}$)
5	263.12	2.11	325.31	47.75	297.12	18.63	343.99	60.85	413.21	75.50	392.45	1.04
10	280.21	3.08	348.41	70.61	305.78	37.78	364.04	73.98	429.39	88.45	400.98	2.39
15	283.18	2.55	360.09	62.80	309.28	38.91	374.49	66.92	443.93	79.39	415.99	2.73
20	291.49	2.13	372.79	62.91	311.82	42.95	389.73	66.19	463.41	77.18	421.07	3.35
30	293.86	1.75	377.87	60.29	318.59	54.03	395.66	64.68	468.49	74.34	433.77	4.07

of the absolute temperature at which a fixed extent of conversion is recorded at different heating rates. Linear plots were computed for α [0.1–0.8] with a 0.1 step. The linear plots of natural logarithm of conversion rate $\ln[\beta/T^2]$ versus $1000/T$ [KAS, Eqn. (1)], $\ln\beta$ versus $1000/T_{plot}$ [FWO, Eqn. (2)] and $\ln[bd_{\alpha}/dt]$ versus $1000/T$ [Friedman, Eqn (3)] corresponding to several degrees of conversion (α) were constructed at five different heating rates which are represented by inclined vertical lines, reflect a linear dependence (Figure 2). The calculated values of the apparent activation energy (kJ mol^{-1}) and frequency factor (min^{-1}), from the slope and intercept, are given in Table 2. These isoconversional plots are parallel straight lines, which indicate a complex weight loss process with several mechanisms. The dependence of the apparent activation energy on the degree of conversion for nonisothermal decomposition process of riboflavin obtained by isoconversional methods is presented in Figure 3. In Figure 3 can be observed a similar trend of curves of E_a versus α and a wide variation corresponding to all applied methods owing to continuous change of decomposition mechanism. It can be observed that E_a decreases throughout the range of conversion, which might suggest a sequence of several reversible partial successive reactions. Also it can be noted that the values of E_a calculated by the KAS and FWO methods are lower than those calculated by the Friedman method. The average values of E_a from the KAS and FWO methods obtained in the range $\alpha[0.1-0.8]$ are also lower than the average values of E_a obtained from Friedman. Although the three model-free methods showed good results, however, Friedman method is not as good as the other two methods. The KAS and FWO methods describe a similar evolution of the apparent activation energy with the degree of conversion. These differences could be due to approximations of the temperature by integral methods (KAS and FWO).

The dependence of the pre-exponential factor ($\ln A$) from all three methods on the degree of conversion is shown in Figure 4. It can be observed that the isoconversional intercept values show a significant dependence on the degree of conversion, that it decreases with the level of conversion, and the highest average value of the isoconversional intercept is observed from the KAS method. Nevertheless, by comparing the applied methods, the lowest and highest values

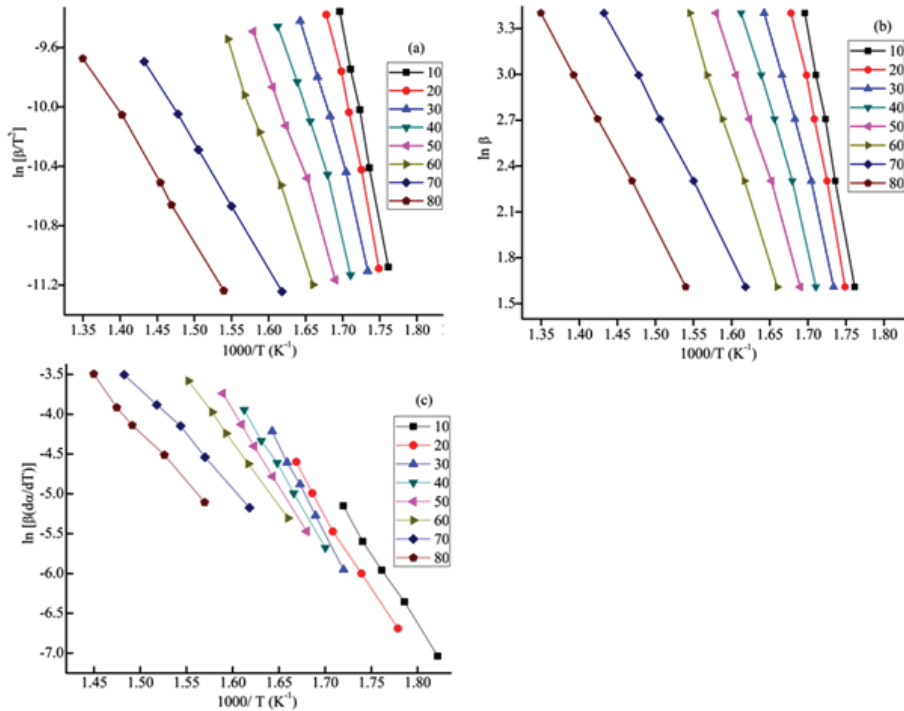


Figure 2 (a)Kissinger–Akahira–Sunose (KAS),(b) Flynn–Wall–Ozawa (FWO) and (c) Friedman plots at varying conversion.

Table 2 Kinetic parameters of riboflavin at different degrees of conversion determined by KAS, FWO and Friedman methods

Conversion (%)	KAS	lnA	FWO	lnA	Friedman	lnA
10	231.73	53.23	233.43	42.42	236.55	43.01
20	201.60	47.21	205.86	35.98	209.45	37.12
30	147.39	35.71	149.47	24.72	152.32	25.93
40	126.66	31.25	129.91	20.28	131.66	21.62
50	119.67	29.54	122.93	18.46	124.24	19.97
60	109.67	27.25	114.12	16.19	116.8	17.77
70	70.05	18.49	76.93	8.58	77.48	9.46
80	15.18	6.63	21.25	-0.78	26.92	-0.870
Average	128.74	31.16	131.73	20.73	134.42	21.7

of the intercept over the whole range of degree of conversion investigated were produced by the FWO and KAS methods, respectively

4. CONCLUSIONS

In this work, the thermal decomposition of riboflavin was studied in a helium atmosphere at five constant heating rates. From TGA and DTG data it was found

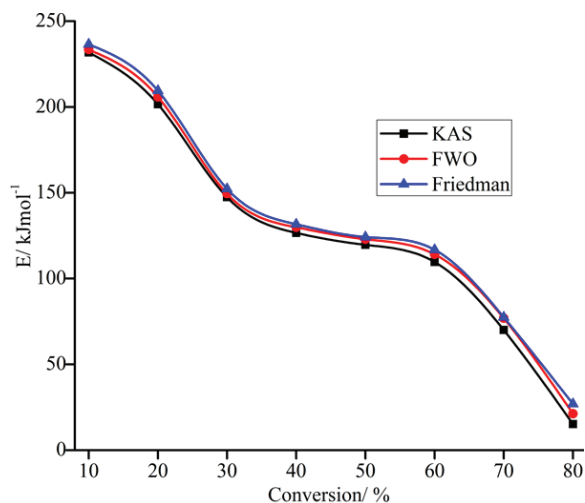


Figure 3 Dependence of apparent activation energy (E_a) on the degree of conversion (α) for nonisothermal decomposition process of riboflavin according to Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO) and Friedman isoconversional methods.

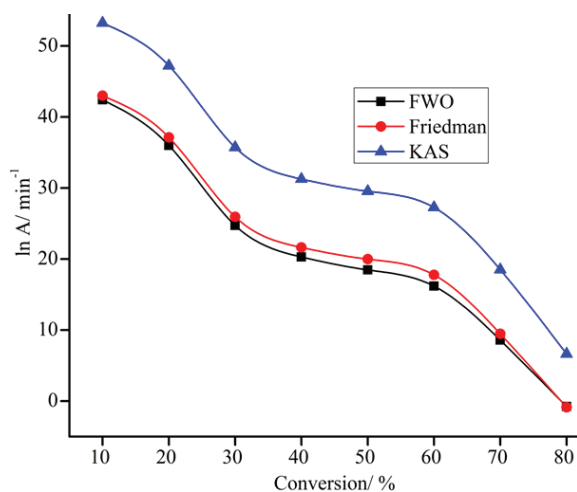


Figure 4 Dependence of isoconversional intercepts on the degree of conversion (α) for nonisothermal decomposition process of riboflavin according to Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO) and Friedman isoconversional methods.

that decomposition proceeds through two stages of weight loss. The kinetic parameters for riboflavin decomposition, i.e. the apparent activation energy and pre-exponential factor, were obtained by the conventional isoconversional methods (two integral [KAS and FWO] and one differential [Friedman] methods). The apparent activation energy and pre-exponential factor calculated by the methods applied over whole range of degrees of conversion (0.1–0.8) showed a similar

trend and a complex reaction mechanism. It was also estimated that the apparent activation energy (E_a) values obtained with KAS are slightly smaller than those determined by FWO and Friedman methods.

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6. REFERENCES

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